

10/538,998 Yong chu 12-27-2006

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closest prior art 2/3

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TERMINAL (ENTER 1, 2, 3, OR ?):2

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truncation
NEWS 7 SEP 25 CA(SM)/Caplus(SM) display of CA Lexicon enhanced
NEWS 8 SEP 25 CAS REGISTRY(SM) no longer includes Concord 3D coordinates
NEWS 9 SEP 25 CAS REGISTRY(SM) updated with amino acid codes for pyrrolysine
NEWS 10 SEP 28 CEABA-VTB classification code fields reloaded with new
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NEWS 21 NOV 20 CA/Caplus to MARPAT accession number crossover limit increased
to 50,000
NEWS 22 DEC 01 CAS REGISTRY updated with new ambiguity codes
NEWS 23 DEC 11 CAS REGISTRY chemical nomenclature enhanced
NEWS 24 DEC 14 WPIDS/WPINDEX/WPIX manual codes updated
NEWS 25 DEC 14 GBFULL and FRFULL enhanced with IPC 8 features and
functionality
NEWS 26 DEC 18 CA/Caplus pre-1967 chemical substance index entries enhanced
with preparation role
NEWS 27 DEC 18 CA/Caplus patent kind codes updated
NEWS 28 DEC 18 MARPAT to CA/Caplus accession number crossover limit increased
to 50,000
NEWS 29 DEC 18 MEDLINE updated in preparation for 2007 reload
NEWS 30 DEC 27 CA/Caplus enhanced with more pre-1907 records

NEWS EXPRESS NOVEMBER 10 CURRENT WINDOWS VERSION IS V8.01c, CURRENT
MACINTOSH VERSION IS V6.0c(ENG) AND V6.0Jc(JP),
AND CURRENT DISCOVER FILE IS DATED 25 SEPTEMBER 2006.

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FILE 'HOME' ENTERED AT 14:54:20 ON 27 DEC 2006

=> file reg

COST IN U.S. DOLLARS

SINCE FILE

TOTAL

ENTRY

SESSION

FULL ESTIMATED COST

0.21

0.21

FILE 'REGISTRY' ENTERED AT 14:54:37 ON 27 DEC 2006

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DICTIONARY FILE UPDATES: 26 DEC 2006 HIGHEST RN 916310-60-6

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=>

Uploading C:\Documents and Settings\ychu\Desktop\Case\10538998\10638998B.str

L1 STRUCTURE UPLOADED

=> d

L1 HAS NO ANSWERS

L1 STR

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

Structure attributes must be viewed using STN Express query preparation.

=> s ll

SAMPLE SEARCH INITIATED 14:55:46 FILE 'REGISTRY'

SAMPLE SCREEN SEARCH COMPLETED - 36 TO ITERATE

100.0% PROCESSED 36 ITERATIONS 18 ANSWERS
SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS: ONLINE **COMPLETE**
BATCH **COMPLETE**
PROJECTED ITERATIONS: 360 TO 1080
PROJECTED ANSWERS: 106 TO 614

L2 18 SEA SSS SAM L1

=> s l1 full
FULL SEARCH INITIATED 14:56:07 FILE 'REGISTRY'
FULL SCREEN SEARCH COMPLETED - 634 TO ITERATE

100.0% PROCESSED 634 ITERATIONS 400 ANSWERS
SEARCH TIME: 00.00.01

L3 400 SEA SSS FUL L1

=> file caplus
COST IN U.S. DOLLARS SINCE FILE TOTAL
ENTRY SESSION
FULL ESTIMATED COST 167.82 168.03

FILE 'CAPLUS' ENTERED AT 14:56:21 ON 27 DEC 2006
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FILE COVERS 1907 - 27 Dec 2006 VOL 146 ISS 1
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=> s l3
L4 1 L3

=> d ibib abs tot

L4 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 2004:589417 CAPLUS
DOCUMENT NUMBER: 141:140320
TITLE: A preparation of insecticidal piperidine and pyridine derivatives
INVENTOR(S): Ding, Ping; Henrie, Robert H., II; Cohen, Daniel H.; Lyga, John W.; Rosen, David S.; Theodoridis, George; Zhang, Qun; Yeager, Walter H.; Donovan, Stephen F.; Zhang, Steven Shunxiang; Shulman, Inna; Yu, Seong Jae; Wang, Guozhi; Zhang, Y. Larry; Gopalsamy, Ariamala; Warkentin, Dennis L.; Rensner, Paul E.; Silverman, Ian

PATENT ASSIGNEE(S): R.; Cullen, Thomas G.
 SOURCE: FMC Corporation, USA
 PCT Int. Appl., 182 pp.
 CODEN: PIXXD2
 DOCUMENT TYPE: Patent
 LANGUAGE: English
 FAMILY ACC. NUM. COUNT: 2
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2004060371	A1	20040722	WO 2003-US38878	20031208
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW RW: BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
AU 2003296308	A1	20040729	AU 2003-296308	20031208
EP 1572207	A1	20050914	EP 2003-814662	20031208
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, HU, SK				
BR 2003017324	A	20051116	BR 2003-17324	20031208
CN 1729178	A	20060201	CN 2003-80106750	20031208
CN 1744895	A	20060308	CN 2003-80109445	20031208
JP 2006516149	T	20060622	JP 2005-508561	20031208
US 2006135504	A1	20060622	US 2005-538998	20051216
PRIORITY APPLN. INFO.:			US 2002-434718P	P 20021218
			US 2003-495059P	P 20030814
			WO 2003-US38878	W 20031208
OTHER SOURCE(S):			MARPAT 141:140320	
GI				

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

AB The invention relates to a prepn. of insecticidal piperidine and pyridine derivs. of formula I [wherein: A is C or CH; B is substituted phenyl; C is O0-1; D is (CH2)0-3; E is a bridging group selected from (CR9R10)-(CR11R12)0-1, (CR9R10)-(CR11R12)0-10, C3H6, C(O), or C(S)NH, etc.; R1 is H, alkyl, alkoxyalkyl, or aryl; R2, R3, R4, R5, and R6 are independently selected from H, halogen, (halo/hydroxy)alkyl, alkylthio, CN, or NO2, etc.; R7 is (halo/hydroxy/alkoxy/dialkylamino)alkyl, sulfonatoalkyl, arylalkyl, or arylcarbonyl, etc.; R8 is H, (cyclo)alkyl, alkoxy, amino, morpholinyl, or indolyl, etc.; R9, R10, R11, and R12 are independently selected from H, alkyl, aryl, etc.]. Prepd. compds. were evaluated for activity against tobacco budworm in a surface-treated diet test. For instance, piperidine deriv. II (compd. 101, insecticidal activity: 100% mortality, 100% growth inhibition) was prepd. via elimination reaction of hydroxymethylpiperidine deriv. III, N-benylation of the obtained methylenepiperidine deriv. IV by 4-nitrophenylmethyl bromide, subsequent redn. of the nitro-group, N-carboxylation of the obtained amine V, and N-oxidn. (example 1).

=> file reg
 COST IN U.S. DOLLARS

SINCE FILE ENTRY TOTAL SESSION

FULL ESTIMATED COST	3.66	171.69
DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)	SINCE FILE	TOTAL
	ENTRY	SESSION
CA SUBSCRIBER PRICE	-0.75	-0.75

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STRUCTURE FILE UPDATES: 26 DEC 2006 HIGHEST RN 916310-60-6
DICTIONARY FILE UPDATES: 26 DEC 2006 HIGHEST RN 916310-60-6

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L5 STRUCTURE UPLOADED

=> d

L5 HAS NO ANSWERS

L5 STR

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

Structure attributes must be viewed using STN Express query preparation.

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SAMPLE SEARCH INITIATED 14:57:53 FILE 'REGISTRY'

SAMPLE SCREEN SEARCH COMPLETED - 490 TO ITERATE

100.0% PROCESSED 490 ITERATIONS

1 ANSWERS

SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS: ONLINE **COMPLETE**

BATCH **COMPLETE**

PROJECTED ITERATIONS: 8472 TO 11128

PROJECTED ANSWERS: 1 TO 80

L6 1 SEA SSS SAM L5

=> s 15 full

FULL SEARCH INITIATED 14:58:00 FILE 'REGISTRY'

FULL SCREEN SEARCH COMPLETED - 9892 TO ITERATE

100.0% PROCESSED 9892 ITERATIONS

14 ANSWERS

SEARCH TIME: 00.00.01

L7 14 SEA SSS FUL L5

=> file caplus

COST IN U.S. DOLLARS

SINCE FILE	TOTAL
ENTRY	SESSION
166.94	338.63

FULL ESTIMATED COST

DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)

SINCE FILE	TOTAL
ENTRY	SESSION
0.00	-0.75

CAS SUBSCRIBER PRICE

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FILE COVERS 1907 - 27 Dec 2006 VOL 146 ISS 1

FILE LAST UPDATED: 26 Dec 2006 (20061226/ED)

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=> s 17

L8 3 L7

=> .d ibib abs tot

L8 ANSWER 1 OF 3 CAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 2004:589417 CAPLUS

DOCUMENT NUMBER: 141:140320

TITLE: A preparation of insecticidal piperidine and pyridine derivatives

INVENTOR(S): Ding, Ping; Henrie, Robert H., II; Cohen, Daniel H.; Lyga, John W.; Rosen, David S.; Theodoridis, George; Zhang, Qun; Yeager, Walter H.; Donovan, Stephen F.; Zhang, Steven Shunxiang; Shulman, Inna; Yu, Seong Jae; Wang, Guozhi; Zhang, Y. Larry; Gopalsamy, Ariamala; Warkentin, Dennis L.; Rensner, Paul E.; Silverman, Ian R.; Cullen, Thomas G.

PATENT ASSIGNEE(S): FMC Corporation, USA

SOURCE: PCT Int. Appl., 182 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent

LANGUAGE: English

FAMILY ACC. NUM. COUNT: 2

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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WO 2004060371	A1	20040722	WO 2003-US38878	20031208
W:	AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW			
RW:	BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG			
AU 2003296308	A1	20040729	AU 2003-296308	20031208
EP 1572207	A1	20050914	EP 2003-814662	20031208
R:	AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, HU, SK			
BR 2003017324	A	20051116	BR 2003-17324	20031208
CN 1729178	A	20060201	CN 2003-80106750	20031208
CN 1744895	A	20060308	CN 2003-80109445	20031208
JP 2006516149	T	20060622	JP 2005-508561	20031208
US 2006135504	A1	20060622	US 2005-538998	20051216
PRIORITY APPLN. INFO.:			US 2002-434718P	P 20021218
			US 2003-495059P	P 20030814
			WO 2003-US38878	W 20031208

OTHER SOURCE(S): MARPAT 141:140320
GI

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

AB The invention relates to a prepn. of insecticidal piperidine and pyridine derivs. of formula I [wherein: A is C or CH; B is substituted phenyl; C is O0-1; D is (CH2)0-3; E is a bridging group selected from (CR9R10)-(CR11R12)0-1, (CR9R10)-(CR11R12)0-10, C3H6, C(O), or C(S)NH, etc.; R1 is H, alkyl, alkoxyalkyl, or aryl; R2, R3, R4, R5, and R6 are independently selected from H, halogen, (halo/hydroxy)alkyl, alkylthio, CN, or NO2, etc.; R7 is (halo/hydroxy/alkoxy/dialkylamino)alkyl, sulfonatoalkyl, arylalkyl, or arylcarbonyl, etc.; R8 is H, (cyclo)alkyl, alkoxy, amino, morpholinyl, or indolyl, etc.; R9, R10, R11, and R12 are independently selected from H, alkyl, aryl, etc.]. Prepd. compds. were evaluated for activity against tobacco budworm in a surface-treated diet test. For instance, piperidine deriv. II (compd. 101, insecticidal activity: 100% mortality, 100% growth inhibition) was prepd. via elimination reaction of hydroxymethylpiperidine deriv. III, N-benzylation of the obtained methylenepiperidine deriv. IV by 4-nitrophenylmethyl bromide, subsequent redn. of the nitro-group, N-carboxylation of the obtained amine V, and N-oxidn. (example 1).

L8 ANSWER 2 OF 3 CAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1964:16612 CAPLUS
DOCUMENT NUMBER: 60:16612
ORIGINAL REFERENCE NO.: 60:2903b-h
TITLE: Phenyl(pyridyl or piperidyl)alkyl benzoates and phenylalkanoates
INVENTOR(S): Rorig, Kurt J.
PATENT ASSIGNEE(S): G.D. Searle and Co.
SOURCE: 10 pp.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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US 3100775	19630813	US 1959-803371	19590401
PRIORITY APPLN. INFO.:		US	19590401

GI For diagram(s), see printed CA Issue.

AB Carbinols of the general formula $RR'ArCR''nOH$, where R is an alkyl or aryl group, R' is a pyridyl or piperidyl group, Ar is an aryl group, R'' is an alkylene group, and n is 0 or 1, are treated with anhydrides of the general formula $(PhRnCO)_2O$, where R is an alkylene group and n is 0 or 1, to give the title compds. which can be used as spasmolytic and fungicidal agents. Thus, a mixt. of .alpha.-phenyl-4-pyridinemethanol 25 and o-ClC₆H₄COCl 60 parts is heated 11 hrs. under N at 130-50.degree., cooled to .apprx.30.degree., treated with excess 10% NaOH, and extd. with ether. The ether ext. is extd. with dil. HCl, the acid ext. made alk. with NaOH, the ppt. sepd. and taken up in ether, the ether mixt. filtered, dried, and evapd., and the residue obtained distd. in vacuo to give .alpha.-phenyl-4-pyridylmethyl o-chlorobenzoate, b0.15 175-95.degree.. Similarly prepd. are the following I (m, n, R, R1, R2, R3, X, X1, X2, X3, X4, m.p., and m.p. HCl salt given): 0, 0, 4-pyridyl, H, H, H, H, H, Cl, H, H, .apprx.68-9.degree. (petr. ether), --; 0, 0, 2-pyridyl, H, H, H, H, H, Cl, H, H, .apprx.76-7.degree. (petr. ether), --; 0, 0, 4-pyridyl, H, H, H, H, H, Cl, Cl, Cl, H, --, 205-7.degree. (EtOH-ether); 0, 0, 4-pyridyl, H, H, H, MeO, H, H, H, H, -- (b0.8 180-215.degree.), --; 0, 0, 4-pyridyl, H, H, H, H, H, MeO, H, H, 94-6.degree. (b0.3 185-205.degree.), --; 0, 0, 4-pyridyl, H, H, H, H, H, EtO, H, H, 96-9.degree. (b0.3 195-200.degree.), --; 0, 1, 4-pyridyl, H, H, H, H, H, MeO, H, H, -- (b0.4 185-215.degree.), --; 0, 0, 4-pyridyl, H, H, H, H, H, MeO, MeO, H, H, --, 210-12.degree.; 0, 0, 4-pyridyl, H, H, H, H, MeO, MeO, MeO, H, 118-20.degree., .apprx.219-20.degree. (EtOH-anhyd. ether) (maleate m. 117-19.degree.); 0, 0, 4-pyridyl, H, H, H, MeO, MeO, MeO, H, H, --, --; 0, 0, 4-pyridyl, H, H, H, MeO, H, MeO, H, MeO, --, --; 0, 0, 4-pyridyl, H, H, H, H, MeO, MeO, MeO, H, --, 202-4.degree.; 0, 0, 2-pyridyl, H, H, H, H, MeO, MeO, MeO, H, 115-16.degree. (iso-PrOH), 172.5.4.degree. (EtOH-ether); 0, 0, 3-pyridyl, H, H, H, H, MeO, MeO, MeO, H, --, 192-4.degree. (EtOH); 1, 0, 4-pyridyl, H, H, H, H, MeO, MeO, MeO, H, --, --; 2, 0, 4-pyridyl, H, H, H, H, MeO, MeO, MeO, H, --, --; 0, 1, 4-pyridyl, H, H, H, H, MeO, MeO, MeO, H, --, 182.degree.; 0, 2, 4-pyridyl, H, H, H, H, MeO, MeO, MeO, H, --, --; 0, 0, 4-pyridyl, H, Me, H, H, MeO, MeO, MeO, H, --, 200-2.degree. (abs. EtOH-ether); 0, 0, 4-pyridyl, H, Me, H, H, EtO, EtO, EtO, H, --, 207-10.degree. (abs. EtOH); 0, 0, 4-pyridyl, H, H, Et, H, EtO, EtO, EtO, H, --, --; 0, 0, 4-pyridyl, H, Cl, H, H, MeO, MeO, MeO, H, --, 204-6.degree. (abs. EtOH); 0, 0, 4-pyridyl, Cl, H, H, H, EtO, EtO, EtO, H, --, --; 0, 0, 4-piperidyl, H, H, H, H, MeO, MeO, MeO, H, --, --; 0, 0, 1-methyl-4-piperidyl, H, H, H, H, MeO, MeO, MeO, H, --, --; 0, 0, 1-octyl-4-piperidyl, H, H, H, H, MeO, MeO, MeO, H, --, --; 0, 0, 1-benzyl-4-piperidyl, H, H, H, H, MeO, MeO, MeO, H, --, -- [HBr salt m. 227-30.degree. (abs. EtOH-ether)]; 0, 0, 4-pyridyl, H, H, H, CO₂H, H, H, H, H, .apprx.201-2.degree., --; 0, 0, 4-pyridyl, H, H, H, CO₂Me, H, H, H, H, --, 96-9.degree.; 0, 0, 4-pyridyl, H, H, H, H, H, CO₂Et, H, H, --, --, 0, 0, 4-pyridyl, H, H, H, NO₂, H, H, H, H, --, --; 0, 0, 4-pyridyl, H, H, H, H, H, NO₂, H, H, --, 224-7.degree.; 0, 0, 4-pyridyl, H, H, H, H, NMe₂, H, H, H, -- (b0.2 200-10.degree.), --; 0, 0, 4-pyridyl, H, H, H, H, H, NET₂, H, H, --, --. Also prepd. were the following (m.p. and m.p. HCl salt given): .alpha.-phenyl-4-pyridinemethyl 3,4,5-trimethoxycinnamate, --, 200-1.degree.; .alpha.-phenyl-4-pyridinemethyl 3,4,5-trimethoxybenzoate N-oxide, --, -- (lambda. 6.72 .mu.); 4-pyridinemethyl 3,3,5-trimethoxybenzoate, --, 210-11.degree. (EtOH); .alpha., .alpha.-diphenyl-4-pyridinemethyl 3,4,5-trimethoxybenzoate, 160.5-1.5.degree. (iso-PrOH), --. Also prepd. are (m.p. given): (3,4,5-Cl₃C₆H₂CO)₂O, 206-10.degree.; .alpha.-m-tolyl-4-pyridinemethanol, 147-50.degree. (C₆H₆); .alpha.-m-chlorophenyl-4-pyridinemethanol, 133-5.degree.; .alpha.-phenyl-4-piperidinemethanol, 168-9.degree. (abs. EtOH); 4-benzoyl-1-methylpyridinium iodide, --; 1-methyl-.alpha.-phenyl-4-piperidinemethanol, --; 4-benzoyl-1-benzylpyridinium chloride, .apprx.193-4.degree. (butanone); 1-benzyl-.alpha.-phenyl-4-

piperidinemethanol-HCl, 190-3.degree. (abs. EtOH-anhyd. ether).

L8 ANSWER 3 OF 3 CAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 1954:28787 CAPLUS

DOCUMENT NUMBER: 48:28787

ORIGINAL REFERENCE NO.: 48:5189d-i,5190a-i,5191a-c

TITLE: Quinolyl ketones. I

AUTHOR(S): de Diesbach, Henri; Pugin, Andre; Morard, Francois;
Nowaczinski, Wojciech; Dessibourg, Joseph

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GI For diagram(s), see printed CA Issue.

AB A no. of quinolyl ketones (I), prepd. by the Skraup synthesis from 4-aminobenzophenones, have been reduced with Raney Ni and H at ordinary pressure and temp. to the tetrahydro derivs. (II) and with (iso-PrO)₃Al to the carbinols (III), but could not be reduced to the tetrahydro carbinols (IV.). Raney Ni reduces III to the methylene derivs. (V) instead of to IV. Thus 6-benzoylquinoline (VI), colorless crystals, m. 60.5.degree. (from ligroine) [VI.H₂O, white plates, m. 39-40.degree. (from MeOH or EtOH); picrate, m. 222.degree.; phenylhydrazone, m. 184.degree.; syn-oxime, m. 198-205.degree.; anti-oxime, m. 192-5.degree.], is prepd. by heating p-H₂NC₆H₄Bz, PhNO₂, glycerol, and concd. H₂SO₄ 3 h. at 160.degree., dilg., treating with steam, acidifying, alkalizing, taking up in Et₂O, filtering, and distg. at 240.degree./16 mm. Similarly are prepd. the following compds. [(a) starting amine, and (b) corresponding quinoline deriv.]: (a) 3,4-Me(H₂N)C₆H₃Bz; (b) 6-benzoyl-8-methylquinoline. (VII), yellowish plates, m. 199.degree. (from AcOH) [phenylhydrazone, m. 235-7.degree. (from C₆H₆)]. (a) 4-Amino-4'-chlorobenzophenone; (b) 6-(p-chlorobenzoyl)quinoline (VIII), m. 204.degree. (from ligroine, b. 120-80.degree., then from MeOH). (a) 4-Amino-2',4'-dichlorobenzophenone, m. 130-1.degree. (100% yield by Raney Ni hydrogenation of the 4-nitro analog in MeOH 24 h. at 100.degree. and 80 atm.); (b) 6-(2,4-dichlorobenzoyl)quinoline (IX), white crystals, m. 131-2.degree.. (a) 4-Amino-2',5'-dichlorobenzophenone, white crystals, m. 123.degree. (from 60% alc.), from the 4-nitro analog with SnCl₂ or Na₂S; (b) 6-(2,5-dichlorobenzoyl)quinoline (X), white needles, m. 134-5.degree. (from dil. alc.) (picrate, m. 208-9.degree.). (a) 4-Amino-3',4'-dichlorobenzophenone, white crystals, m. 161-2.degree. (from alc.), from the 4-nitro compd. with SnCl₂; (b) 6-(3,4-dichlorobenzoyl)quinoline (XI), m. 139-40.degree. (from ligroine and MeOH) (picrate, m. 173-4.degree.). (a) 4-Amino-4'-chlorobenzophenone; (b) 6-(4-chlorobenzyl)quinoline, m. 191.5-2.degree. (from alc.). (a) 4-Amino-2',4'-dichlorodiphenylmethane, blue crystals, m. 102-3.degree. (Ac deriv., m. 141-2.degree.), from the 4-nitro compd. with SnCl₂; (b) 6-(2,4-dichlorobenzyl)quinoline (in poor yield) (picrate, m. 167-8.degree.). (a) 4-Amino-3',4'-dichlorodiphenylmethane, an oil (Bz deriv., m. 106-7.degree.), from the 4-nitro compd. and SnCl₂; (b) 6-(3,4-dichlorobenzyl)quinoline (picrate, m. 164-5.degree.). 6-Acetyl-1,2,3,4-tetrahydroquinoline (XII), greenish plates, m. 105-7.degree. (picrate, m. 125.degree.; oxime, m. 144.degree.), is prepd. by condensing 1-acetyl-1,2,3,4-tetrahydroquinoline with ClCH₂COCl at room temp., sapong. the 1-Ac group with boiling 20% HCl, and heating in 80% alc. with powd. Fe and 2N HCl; heated 5 h. at 188.degree. in a sealed tube with Hg(OAc)₂, AcOH, and H₂O it gives yellowish prisms of 6-acetylquinoline, m. 75-6.degree. (picrate, m. 242.degree.). A Beckmann rearrangement of XII oxime gives 6-amino-1,2,3,4-tetrahydroquinoline, m. 95.5-6.degree.. Na redn. of Quinaldine in AmOH gives 93% 1,2,3,4-tetrahydroquinaldine, acetylated with Ac₂O to the 1-Ac deriv., b₁₂ 153.degree., yellow crystals, m. 57.degree.; which, treated with ClCH₂COCl in CS₂, then slowly with AlCl₃, and let stand 2 days yields 6-(chloroacetyl)-1,2,3,4-tetrahydroquinaldine-HCl, white crystals, m.

225-6.degree., converted by neutralization with dil. alkali to the free quinaldine, yellow crystals, m. 121.degree., which is dechlorinated in 80% HCl with Fe and 2N HCl to 6-acetyl-1,2,3,4-tetrahydroquinaldine, m. 69.degree.. The following 1,2,3,4-tetrahydroquinolines are prepd. in good yield by hydrogenating 5 g. of the appropriate I in 50 mL. MeOH at room temp. and pressure in the presence of Raney Ni, warming, filtering, washing the Ni with warm MeOH, evapg. to a small vol., and recrystg.: 6-benzoyl (XIII), yellowish crystals, m. 113.degree. [1-ON deriv., m. 119-20.degree.; 1-Bz deriv., m. 131.degree. (from 50% AcOH); 1-Ac deriv., m. 97.degree. (from dil. alc.)]; 6-benzoyl-8-Me, pale yellow needles, m. 118.degree.; 6-(p-chlorobenzoyl)tetrahydroquinoline, m. 156.degree. (1-ON deriv., m. 173-4.degree.; 6-Bz deriv., m. 146.degree.); 6-(2,4-dichlorobenzoyl), m. 137.degree. (1-ON deriv., m. 145.degree.); 6-(2,5-dichlorobenzoyl), m. 153.degree.. The Meerwein-Ponndorf redn. of I to III is carried out in nearly 100% yield by adding 10 g. of the I in 30 mL. iso-PrOH to (iso-PrO)3Al (made by refluxing 2.5 g. Al paste 10 h. with 0.125 g. HgCl2 in 50 mL. abs. iso-PrOH), slowly distg. the Me2CO formed, alkalinizing, steam-distg. the iso-PrOH, adding boiling H2O to the residue, and crystg. from dil. alc. Thus are prepd. the following carbinols: phenyl(6-quinolyl) (XIV), m. 127-8.degree. (picrate, m. 190.degree.; picrate of the acetate (ester), m. 188.degree.); phenyl(8-methyl-6-quinolyl) (XV), m. 133.degree. [picrate, m. 202-3.degree.; acetate (ester), m. 100.degree. (from dil. alc.)]; (p-chlorophenyl)(6-quinolyl), m. 153.degree. (picrate, m. 186.degree.; picrate of the acetate (ester), m. 209.degree.); (2,4-dichlorophenyl)(6-quinolyl), m. 161.degree. (picrate, m. 225.degree.; acetate (ester), m. 125-6.degree.; picrate of the acetate, m. 212.degree.); X, (2, 5-dichlorophenyl)(6-quinolyl), m. 161.degree. (acetate (ester), m. 174.degree.); (3,4-dichlorophenyl)(6-quinolyl), m. 145.degree. (picrate of the acetate (ester), m. 189-90.degree.). Raney Ni hydrogenation of XIV gives 6-benzylquinoline, white crystals, m. 48-9.degree.; similarly XV is reduced to 6-benzyl-8-methylquinoline, m. 55.degree.. An attempted (iso-PrO)3Al redn. of XIII to the corresponding IV gives instead a white paste, m. 120-40.degree., sol. in C6H6 and CHCl3, slightly sol. in alc. 2-Benzoylquinoline is reduced by (iso-PrO)3Al in 100% yield to phenyl(2-quinolyl)carbinol (XVI), white crystals, m. 69.degree. (from ligroine); also obtained by Raney Ni hydrogenation at room pressure and temp. [picrate, yellow crystals, m. 138.degree. (from alc.)], instead of to the tetrahydro deriv. Phenyl(1,2,3,4-tetrahydro-2-quinalyl)carbinol, b0.005 140.degree. [1-ON deriv., yellow plates, m. 103.degree. (from dil. alc.); N,O-di-Bz deriv., m. 161.degree. (from ligroine)], is prepd. by reducing 2 g. 2-benzoylquinoline 1 h. in 300 g. MeOH with H at 70.degree. and 50 atm. in the presence of Raney Ni, filtering, washing with MeOH, evapg. to a small vol., dilg. with H2O, adding Et2O, and vacuum-distg. the oil. 4-Benzoylquinoline is reduced by (iso-PrO)3Al to phenyl(4-quinolyl)carbinol, m. 127.degree. (from dil. alc.) (acetate (ester), white plates, m. 100.degree.), and by Raney Ni hydrogenation at 100.degree. and 70 atm. to phenyl(1,2,3,4-tetrahydro-4-quinolyl)carbinol, m. 135.degree. (from dil. alc.), b0.001 110-15.degree. [1-ON deriv., yellow leaves, m. 105.degree. (from dil. ac.); N,O-di-Bz deriv., m. 156.degree. (from ligroine)]. 2-Methyl-4-benzoylquinoline (XVII), bright plates, m. 118.degree. (from ligroine), is prepd. by heating 2 g. 2-methyl-4-quinolinecarboxamide in 30 mL. POCl3 with 3 g. PCl5 (with 2 drops water added to start the reaction) 15-20 min. at 110.degree., cooling with ice, neutralizing, extg. with Et2O, crystg. from ligroine the 2-methyl-4-cyanoquinoline (XVIII), white needles, m. 106.degree., and adding the Grignard reagent from 12 g. PhBr and 2 g. Mg in 30 mL. Et2O to 5 g. XVIII in 50 mL. Et2O; XVII is reduced by (iso-Pr)3Al to phenyl(2-methyl-4-quinolyl)carbinol, colorless prisms, m. 167.degree. (from dil. alc.) [acetate (ester), m. 103.degree. (from dil. alc.)], and by Raney Ni hydrogenation at 100.degree. and 70 atm. to phenyl(2-methyl-1,2,3,4-tetrahydro-4-quinolyl)carbinol, m. 162.degree. (from dil. alc.), b0.001 130.degree. [N,O-Bz deriv., m. 149.degree. (from ligroine)]. Raney Ni redn. at room pressure and temp. of

8-benzoylquinoline gives at once phenyl(1,2 3,4-tetrahydro-8-quinolyl)carbinol, oil, b0.001 120.degree. [1-ON deriv., yellow prisms, m. 146.degree. (from alc.), (di-Bz deriv., m. 132.degree. (from ligroine))]. Nitration of 6 g. VI in 25 mL. concd. H2SO4 with 1 mL. nitrating mixt. (= 0.255 g. HNO3) added at -10.degree., followed by cooling with ice, filtering, neutralizing with NH4OH, and crystg. in alc., gives 6-(m-nitrobenzoyl)quinoline, yellow needles, m. 160.degree., which reduced by SnCl2 in alc. to the amino compd., yellow crystals, m. 142.degree. (from H2O). Similarly, VII is nitrated to 6-(m-nitrobenzoyl)-8-methylquinoline, m. 156.degree., which is reduced to the 3-amino compd., yellow crystals, m. 187.degree. (from ligroine). The (dichlorobenzoyl)quinolines cannot be nitrated.

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L8 ANSWER 2 OF 3 CAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 1964:16612 CAPLUS

DOCUMENT NUMBER: 60:16612

ORIGINAL REFERENCE NO.: 60:2903b-h

TITLE: Phenyl(pyridyl or piperidyl)alkyl benzoates and phenylalkanoates

INVENTOR(S): Rorig, Kurt J.

PATENT ASSIGNEE(S): G.D. Searle and Co.

SOURCE: 10 pp.

DOCUMENT TYPE: Patent

LANGUAGE: Unavailable

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

closest prior art

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 3100775		19630813	US 1959-803371	19590401
PRIORITY APPLN. INFO.:			US	19590401

GI For diagram(s), see printed CA Issue.

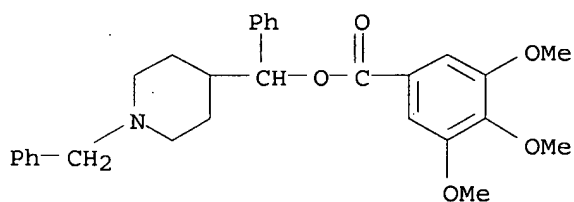
AB Carbinols of the general formula RR'ArCR''nOH, where R is an alkyl or aryl group, R' is a pyridyl or piperidyl group, Ar is an aryl group, R'' is an alkylene group, and n is 0 or 1, are treated with anhydrides of the general formula (PhRnCO)2O, where R is an alkylene group and n is 0 or 1, to give the title compds. which can be used as spasmolytic and fungicidal agents. Thus, a mixt. of .alpha.-phenyl-4-pyridinemethanol 25 and o-ClC6H4COCl 60 parts is heated 11 hrs. under N at 130-50.degree., cooled to .apprx.30.degree., treated with excess 10% NaOH, and extd. with ether. The ether ext. is extd. with dil. HCl, the acid ext. made alk. with NaOH, the ppt. sepd. and taken up in ether, the ether mixt. filtered, dried, and evapd., and the residue obtained distd. in vacuo to give .alpha.-phenyl-4-pyridylmethyl o-chlorobenzoate, b0.15 175-95.degree.. Similarly prepd. are the following I (m, n, R, R1, R2, R3, X, X1, X2, X3, X4, m.p., and m.p. HCl salt given): 0, 0, 4-pyridyl, H, H, H, H, H, Cl, H, H, .apprx.68-9.degree. (petr. ether), --; 0, 0, 2-pyridyl, H, H, H, H, H, Cl, H, H, .apprx.76-7.degree. (petr. ether), --; 0, 0, 4-pyridyl, H, H, H, H, Cl, Cl, Cl, H, --, 205-7.degree. (EtOH-ether); 0, 0, 4-pyridyl, H, H, H, MeO, H, H, H, H, -- (b0.8 180-215.degree.), --; 0, 0, 4-pyridyl, H, H, H, H, H, MeO, H, H, 94-6.degree. (b0.3 185-205.degree.), --; 0, 0, 4-pyridyl, H, H, H, H, H, EtO, H, H, 96-9.degree. (b0.3 195-200.degree.), --; 0, 1, 4-pyridyl, H, H, H, H, H, MeO, H, H, -- (b0.4 185-215.degree.), --; 0, 0, 4-pyridyl, H, H, H, H, MeO, MeO, H, H, --, 210-12.degree.; 0, 0, 4-pyridyl, H, H, H, H, MeO, MeO, MeO, H, 118-20.degree., .apprx.219-20.degree. (EtOH-anhyd. ether) (maleate m. 117-19.degree.); 0, 0, 4-pyridyl, H, H, H, MeO, MeO, MeO, H, H, --, --; 0, 0, 4-pyridyl, H, H, H, MeO, H, MeO, H, MeO, --, --; 0, 0, 4-pyridyl, H, H, H, H, MeO, MeO, MeO, H, --, 202-4.degree.; 0, 0, 2-pyridyl, H, H, H, H, MeO, MeO, MeO, H, 115-16.degree. (iso-PROH), 172.5.4.degree. (EtOH-ether); 0, 0, 3-pyridyl, H, H, H, H, MeO, MeO, MeO, H, --, 192-4.degree. (EtOH); 1, 0, 4-pyridyl,

H, H, H, H, MeO, MeO, MeO, H, --, --; 2, 0, 4-pyridyl, H, H, H, H, MeO, MeO, MeO, H, --, --; 0, 1, 4-pyridyl, H, H, H, H, MeO, MeO, MeO, H, --, 182.degree.; 0, 2, 4-pyridyl, H, H, H, H, MeO, MeO, MeO, H, --, --; 0, 0, 4-pyridyl, H, Me, H, H, MeO, MeO, MeO, H, --, 200-2.degree. (abs. EtOH-ether); 0, 0, 4-pyridyl, H, Me, H, H, EtO, EtO, EtO, H, --, 207-10.degree. (abs. EtOH); 0, 0, 4-pyridyl, H, H, Et, H, EtO, EtO, EtO, H, --, --; 0, 0, 4-pyridyl, H, Cl, H, H, MeO, MeO, MeO, H, --, 204-6.degree. (abs. EtOH); 0, 0, 4-pyridyl, Cl, H, H, H, EtO, EtO, EtO, H, --, --; 0, 0, 4-piperidyl, H, H, H, H, MeO, MeO, MeO, H, --, --; 0, 0, 1-methyl-4-piperidyl, H, H, H, H, MeO, MeO, MeO, H, --, --; 0, 0, 1-octyl-4-piperidyl, H, H, H, H, MeO, MeO, MeO, H, --, --; 0, 0, 1-benzyl-4-piperidyl, H, H, H, H, MeO, MeO, MeO, H, --, -- [HBr salt m. 227-30.degree. (abs. EtOH-ether)]; 0, 0, 4-pyridyl, H, H, H, CO₂H, H, H, H, H, .apprx.201-2.degree., --; 0, 0, 4-pyridyl, H, H, H, CO₂Me, H, H, H, H, --, 96-9.degree.; 0, 0, 4-pyridyl, H, H, H, H, H, CO₂Et, H, H, --, --, 0, 0, 4-pyridyl, H, H, H, NO₂, H, H, H, H, --, --; 0, 0, 4-pyridyl, H, H, H, H, H, NO₂, H, H, --, 224-7.degree.; 0, 0, 4-pyridyl, H, H, H, H, H, NMe₂, H, H, H, -- (b0.2 200-10.degree.), --; 0, 0, 4-pyridyl, H, H, H, H, H, NEt₂, H, H, --, --. Also prepd. were the following (m.p. and m.p. HCl salt given): .alpha.-phenyl-4-pyridinemethyl 3,4,5-trimethoxycinnamate, --, 200-1.degree.; .alpha.-phenyl-4-pyridinemethyl 3,4,5-trimethoxybenzoate N-oxide, --, -- (.lambda. 6.72 .mu.); 4-pyridinemethyl 3,3,5-trimethoxybenzoate, --, 210-11.degree. (EtOH); .alpha., .alpha.-diphenyl-4-pyridinemethyl 3,4,5-trimethoxybenzoate, 160.5-1.5.degree. (iso-PrOH), --. Also prepd. are (m.p. given): (3,4,5-Cl₃C₆H₂CO)₂O, 206-10.degree.; .alpha.-m-tolyl-4-pyridinemethanol, 147-50.degree. (C₆H₆); .alpha.-m-chlorophenyl-4-pyridinemethanol, 133-5.degree.; .alpha.-phenyl-4-piperidinemethanol, 168-9.degree. (abs. EtOH); 4-benzoyl-1-methylpyridinium iodide, --; 1-methyl-.alpha.-phenyl-4-piperidinemethanol, --; 4-benzoyl-1-benzylpyridinium chloride, .apprx.193-4.degree. (butanone); 1-benzyl-.alpha.-phenyl-4-piperidinemethanol-HCl, 190-3.degree. (abs. EtOH-anhyd. ether).

IT 98023-55-3P, 4-Piperidinemethanol, 1-benzyl-.alpha.-phenyl-, 3,4,5-trimethoxybenzoate, hydrobromide
 RL: PREP (Preparation)
 (prepn. of)

RN 98023-55-3 CAPLUS

CN Benzoic acid, 3,4,5-trimethoxy-, .alpha.-(1-benzyl-4-piperidyl)benzyl ester, hydrobromide (6CI, 7CI) (CA INDEX NAME)



● HBr

L8 ANSWER 3 OF 3 CAPLUS COPYRIGHT 2006 ACS on STN
 ACCESSION NUMBER: 1954:28787 CAPLUS
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 ORIGINAL REFERENCE NO.: 48:5189d-i,5190a-i,5191a-c
 TITLE: Quinolyl ketones. I
 AUTHOR(S): de Diesbach, Henri; Pugin, Andre; Morard, Francois;
 Nowaczinski, Wojceich; Dessibourg, Joseph
 CORPORATE SOURCE: Univ. Fribourg, Switz.
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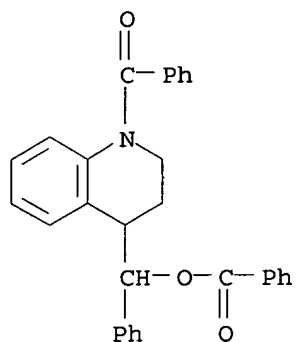
GI For diagram(s), see printed CA Issue.

AB A no. of quinolyl ketones (I), prepd. by the Skraup synthesis from 4-aminobenzophenones, have been reduced with Raney Ni and H at ordinary pressure and temp. to the tetrahydro derivs. (II) and with (iso-PrO)₃Al to the carbinols (III), but could not be reduced to the tetrahydro carbinols (IV.). Raney Ni reduces III to the methylene derivs. (V) instead of to IV. Thus 6-benzoylquinoline (VI), colorless crystals, m. 60.5.degree. (from ligroine) [VI.H₂O, white plates, m. 39-40.degree. (from MeOH or EtOH); picrate, m. 222.degree.; phenylhydrazone, m. 184.degree.; syn-oxime, m. 198-205.degree.; anti-oxime, m. 192-5.degree.], is prepd. by heating p-H₂NC₆H₄Bz, PhNO₂, glycerol, and concd. H₂SO₄ 3 h. at 160.degree., dilg., treating with steam, acidifying, alkalizing, taking up in Et₂O, filtering, and distg. at 240.degree./16 mm. Similarly are prepd. the following compds. [(a) starting amine, and (b) corresponding quinoline deriv.]: (a) 3,4-Me(H₂N)C₆H₃Bz; (b) 6-benzoyl-8-methylquinoline. (VII), yellowish plates, m. 199.degree. (from AcOH) [phenylhydrazone, m. 235-7.degree. (from C₆H₆)]. (a) 4-Amino-4'-chlorobenzophenone; (b) 6-(p-chlorobenzoyl)quinoline (VIII), m. 204.degree. (from ligroine, b. 120-80.degree., then from MeOH). (a) 4-Amino-2',4'-dichlorobenzophenone, m. 130-1.degree. (100% yield by Raney Ni hydrogenation of the 4-nitro analog in MeOH 24 h. at 100.degree. and 80 atm.); (b) 6-(2,4-dichlorobenzoyl)quinoline (IX), white crystals, m. 131-2.degree.. (a) 4-Amino-2',5'-dichlorobenzophenone, white crystals, m. 123.degree. (from 60% alc.), from the 4-nitro analog with SnCl₂ or Na₂S; (b) 6-(2,5-dichlorobenzoyl)quinoline (X), white needles, m. 134-5.degree. (from dil. alc.) (picrate, m. 208-9.degree.). (a) 4-Amino-3',4'-dichlorobenzophenone, white crystals, m. 161-2.degree. (from alc.), from the 4-nitro compd. with SnCl₂; (b) 6-(3,4-dichlorobenzoyl)quinoline (XI), m. 139-40.degree. (from ligroine and MeOH) (picrate, m. 173-4.degree.). (a) 4-Amino-4'-chlorobenzophenone; (b) 6-(4-chlorobenzyl)quinoline, m. 191.5-2.degree. (from alc.). (a) 4-Amino-2',4'-dichlorodiphenylmethane, blue crystals, m. 102-3.degree. (Ac deriv., m. 141-2.degree.), from the 4-nitro compd. with SnCl₂; (b) 6-(2,4-dichlorobenzyl)quinoline (in poor yield) (picrate, m. 167-8.degree.). (a) 4-Amino-3',4'-dichlorodiphenylmethane, an oil (Bz deriv., m. 106-7.degree.), from the 4-nitro compd. and SnCl₂; (b) 6-(3,4-dichlorobenzyl)quinoline (picrate, m. 164-5.degree.). 6-Acetyl-1,2,3,4-tetrahydroquinoline (XII), greenish plates, m. 105-7.degree. (picrate, m. 125.degree.; oxime, m. 144.degree.), is prepd. by condensing 1-acetyl-1,2,3,4-tetrahydroquinoline with ClCH₂COCl at room temp., sapong. the 1-Ac group with boiling 20% HCl, and heating in 80% alc. with powd. Fe and 2N HCl; heated 5 h. at 188.degree. in a sealed tube with Hg(OAc)₂, AcOH, and H₂O it gives yellowish prisms of 6-acetylquinoline, m. 75-6.degree. (picrate, m. 242.degree.). A Beckmann rearrangement of XII oxime gives 6-amino-1,2,3,4-tetrahydroquinoline, m. 95.5-6.degree.. Na redn. of Quinaldine in AmOH gives 93% 1,2,3,4-tetrahydroquinaldine, acetylated with Ac₂O to the 1-Ac deriv., b₁₂ 153.degree., yellow crystals, m. 57.degree.; which, treated with ClCH₂COCl in CS₂, then slowly with AlCl₃, and let stand 2 days yields 6-(chloroacetyl)-1,2,3,4-tetrahydroquinaldine-HCl, white crystals, m. 225-6.degree., converted by neutralization with dil. alkali to the free quinaldine, yellow crystals, m. 121.degree., which is dechlorinated in 80% HCl with Fe and 2N HCl to 6-acetyl-1,2,3,4-tetrahydroquinaldine, m. 69.degree.. The following 1,2,3,4-tetrahydroquinolines are prepd. in good yield by hydrogenating 5 g. of the appropriate I in 50 mL. MeOH at room temp. and pressure in the presence of Raney Ni, warming, filtering, washing the Ni with warm MeOH, evapg. to a small vol., and recrystg.: 6-benzoyl (XIII), yellowish crystals, m. 113.degree. [1-ON deriv., m. 119-20.degree.; 1-Bz deriv., m. 131.degree. (from 50% AcOH); 1-Ac deriv., m. 97.degree. (from dil. alc.)]; 6-benzoyl-8-Me, pale yellow needles, m. 118.degree.; 6-(p-chlorobenzoyl)tetrahydroquinoline, m. 156.degree. (1-ON

deriv., m. 173-4.degree.; 6-Bz deriv., m. 146.degree.);
6-(2,4-dichlorobenzoyl), m. 137.degree. (1-ON deriv., m. 145.degree.);
6-(2,5-dichlorobenzoyl), m. 153.degree.. The Meerwein-Ponndorf redn. of I
to III is carried out in nearly 100% yield by adding 10 g. of the I in 30
mL. iso-PrOH to (iso-PrO)3Al (made by refluxing 2.5 g. Al paste 10 h. with
0.125 g. HgCl2 in 50 mL. abs. iso-PrOH), slowly distg. the Me2CO formed,
alkalizing, steam-distg. the iso-PrOH, adding boiling H2O to the residue,
and crystg. from dil. alc. Thus are prepd. the following carbinols:
phenyl(6-quinolyl) (XIV), m. 127-8.degree. (picrate, m. 190.degree.;
picrate of the acetate (ester), m. 188.degree.); phenyl(8-methyl-6-
quinolyl) (XV), m. 133.degree. [picrate, m. 202-3.degree.; acetate
(ester), m. 100.degree. (from dil. alc.)]; (p-chlorophenyl)(6-quinolyl),
m. 153.degree. (picrate, m. 186.degree.; picrate of the acetate (ester),
m. 209.degree.); (2,4-dichlorophenyl)(6-quinolyl), m. 161.degree.
(picrate, m. 225.degree.; acetate (ester), m. 125-6.degree.; picrate of
the acetate, m. 212.degree.); X, (2, 5-dichlorophenyl)(6-quinolyl), m.
161.degree. (acetate (ester), m. 174.degree.); (3,4-dichlorophenyl)(6-
quinolyl), m. 145.degree. (picrate of the acetate (ester), m.
189-90.degree.). Raney Ni hydrogenation of XIV gives 6-benzylquinoline,
white crystals, m. 48-9.degree.; similarly XV is reduced to
6-benzyl-8-methylquinoline, m. 55.degree.. An attempted (iso-PrO)3Al
redn. of XIII to the corresponding IV gives instead a white paste, m.
120-40.degree., sol. in C6H6 and CHCl3, slightly sol. in alc.
2-Benzoylquinoline is reduced by (iso-PrO)3Al in 100% yield to
phenyl(2-quinolyl)carbinol (XVI), white crystals, m. 69.degree. (from
ligroine); also obtained by Raney Ni hydrogenation at room pressure and
temp. [picrate, yellow crystals, m. 138.degree. (from alc.)], instead of
to the tetrahydro deriv. Phenyl(1,2,3,4-tetrahydro-2-quinolyl)carbinol,
b0.005 140.degree. [1-ON deriv., yellow plates, m. 103.degree. (from dil.
alc.); N,O-di-Bz deriv., m. 161.degree. (from ligroine)], is prepd. by
reducing 2 g. 2-benzoylquinoline 1 h. in 300 g. MeOH with H at 70.degree.
and 50 atm. in the presence of Raney Ni, filtering, washing with MeOH,
evapg. to a small vol., dilg. with H2O, adding Et2O, and vacuum-distg. the
oil. 4-Benzoylquinoline is reduced by (iso-PrO)3Al to
phenyl(4-quinolyl)carbinol, m. 127.degree. (from dil. alc.) (acetate
(ester), white plates, m. 100.degree.), and by Raney Ni hydrogenation at
100.degree. and 70 atm. to phenyl(1,2,3,4-tetrahydro-4-quinolyl)carbinol,
m. 135.degree. (from dil. alc.), b0.001 110-15.degree. [1-ON deriv.,
yellow leaves, m. 105.degree. (from dil. alc.); N,O-di-Bz deriv., m.
156.degree. (from ligroine)]. 2-Methyl-4-benzoylquinoline (XVII), bright
plates, m. 118.degree. (from ligroine), is prepd. by heating 2 g.
2-methyl-4-quinolinecarboxamide in 30 mL. POCl3 with 3 g. PCl5 (with 2
drops water added to start the reaction) 15-20 min. at 110.degree.,
cooling with ice, neutralizing, extg. with Et2O, crystg. from ligroine the
2-methyl-4-cyanoquinoline (XVIII), white needles, m. 106.degree., and
adding the Grignard reagent from 12 g. PhBr and 2 g. Mg in 30 mL. Et2O to
5 g. XVIII in 50 mL. Et2O; XVII is reduced by (iso-Pr)3Al to
phenyl(2-methyl-4-quinolyl)carbinol, colorless prisms, m. 167.degree.
(from dil. alc.) [acetate (ester), m. 103.degree. (from dil. alc.)], and
by Raney Ni hydrogenation at 100.degree. and 70 atm. to
phenyl(2-methyl-1,2,3,4-tetrahydro-4-quinolyl)carbinol, m. 162.degree.
(from dil. alc.), b0.001 130.degree. [N,O-Bz deriv., m. 149.degree. (from
ligroine)]. Raney Ni redn. at room pressure and temp. of
8-benzoylquinoline gives at once phenyl(1,2,3,4-tetrahydro-8-
quinolyl)carbinol, oil, b0.001 120.degree. [1-ON deriv., yellow prisms, m.
146.degree. (from alc.), (di-Bz deriv., m. 132.degree. (from ligroine))].
Nitration of 6 g. VI in 25 mL. concd. H2SO4 with 1 mL. nitrating mixt. (= 0.255 g. HNO3) added at -10.degree., followed by cooling with ice,
filtering, neutralizing with NH4OH, and crystg. in alc., gives
6-(m-nitrobenzoyl)quinoline, yellow needles, m. 160.degree., which reduced
by SnCl2 in alc. to the amino compd., yellow crystals, m. 142.degree.
(from H2O). Similarly, VII is nitrated to 6-(m-nitrobenzoyl)-8-
methylquinoline, m. 156.degree., which is reduced to the 3-amino compd.,
yellow crystals, m. 187.degree. (from ligroine). The

(dichlorobenzoyl)quinolines cannot be nitrated.

IT 858473-25-3P, 4-Quinolinemethanol, 1-benzoyl-1,2,3,4-tetrahydro-
.alpha.-phenyl-, benzoate 858473-28-6P, 4-Quinolinemethanol,
1-benzoyl-1,2,3,4-tetrahydro-2-methyl-.alpha.-phenyl-, benzoate
RL: PREP (Preparation)
(prepn. of)
RN 858473-25-3 CAPLUS
CN 4-Quinolinemethanol, 1-benzoyl-1,2,3,4-tetrahydro-.alpha.-phenyl-,
benzoate (5CI) (CA INDEX NAME)



RN 858473-28-6 CAPLUS
CN 4-Quinolinemethanol, 1-benzoyl-1,2,3,4-tetrahydro-2-methyl-.alpha.-phenyl-,
benzoate (5CI) (CA INDEX NAME)

